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In this article, we calculate pseudocontact shifts for tetragonal high-spin Co(II) complexes using a crystal field model. Calculated results for the dipolar field strength and its variation with temperature are compared with values derived from experimental measurements on complexes of the form $Co(CH_3OH)_5X^{2+}$. The calculation involves evaluation of the anisotropy of the magnetic susceptibility, and proceeds by the following steps: (a) from the crystal field parameters *Dq*, *Ds*, *Dt*, and *B* the three orbital wave functions of lowest energy are found. (b) The effect of spin–orbit coupling over the 12 states (three orbital wave functions coupled with four spin states) is evaluated. (c) The parallel and perpendicular components of the magnetic susceptibility are calculated, considering only these 12 states but taking into account thermal populations. It is shown that good numerical agreement can be obtained with experimental results for the dipole field strength and its temperature dependence. However, the calculations show that the linearity found when pseudocontact shifts are plotted against reciprocal temperature is only apparent, making simple interpretations, or extrapolation of the plots so obtained, meaningless.

I. Introduction

The pseudocontact or dipolar shift, caused by the proximity to the nucleus studied of a paramagnetic center in an anisotropic environment, has recently been an extremely active field of research, both theoretical and experimental.[1] Much of this work involves the use of the pseudocontact shift and "shift reagents" in studies of molecular structure and bonding. However, it has been emphasized by many authors in this field that pseudocontact shift studies are often fraught with ambiguity, so that theoretical studies which can be of help in adding to our understanding of the effect are still welcome.

Recent studies by Vriesenga and coworkers[2] measured contact NMR shifts for the cis and trans methanol methyl resonances of a series of $Co(CH_3OH)_5X^{2+}$ complexes. In these systems, many of the ambiguities connected with interpretation of the spectra and of the shifts, which enter other studies, are absent. We have discussed a method[3] of separating the observed shifts into Fermi contact and pseudocontact contributions. The pseudocontact shift for nucleus i is given as

$$\nu_i^{D} = -D\left\langle \frac{3\cos^2\chi_i - 1}{r_i^3} \right\rangle \nu_0 \qquad (1)$$

where the triangular bracket is the average over internal vibrations and rotations of a factor depending on the location of nucleus i relative to the paramagnetic center. (Here, ν_0 is the resonance frequency, 100 MHz.) By calculating this, we derived values of D for the $Co(CH_3OH)_5X^{2+}$ complexes.

Subsequently, experimental information was obtained on D as a function of temperature.[4] Some of this data are given in section V (see eq 22 and Table II). The apparent straight lines obtained when D was plotted against $1/T$ suggested a simple qualitative explanation of the pseudocontact shifts in terms of a crystal field model for the paramagnetic ion. The value of D depends on the anisotropy of the magnetic susceptibility of this ion. Normally, magnetic susceptibilities consist of a term proportional to $1/T$ (the "g factor" term) and a term independent of T (the "high-frequency" term). Both are calculable within the crystal field model. Furthermore, plots of shifts ν_i^{D} for cis and trans protons vs. $1/T$, extrapolated to low values of $1/T$, crossed for positive values of $1/T$.

We now believe that the thermal population of excited levels is important, and that the straight lines on the ν_i^{D} vs. $1/T$ plots are only apparent, so that extrapolation to a crossing point is not meaningful. However, calculations with the crystal field model using reasonable values for the parameters led to values in accord with experiment for D and its variation with temperature for the region for which experimental measurements were made.

This means that, at least in the present case, pseudocontact shifts can be explained in a crystal field framework. It should be emphasized that the number and quality of measured shifts, plus the simple and well-known geometries of the methanol complexes, make the available information on D more reliable and extensive than for most other systems studied. Obtaining exact agreement with experiment is not our principal goal, since the exact values of the parameters used in the calculation cannot be determined independently. Thus, only a few complete calculations are given.

We are more interested in explaining the signs, magnitudes, and temperature dependencies of the shifts in different $Co(CH_3OH)_5X^{2+}$ complexes. As late as 1971, Forster[5] could note that, while the importance of the pseudocontact contributions to NMR shifts of Co complexes had been clearly demonstrated, the explanation of the signs and magnitudes of the shifts was as yet lacking.

Of course, other calculations of D for various systems have been performed. Gerloch and Mackey[6] performed calculations of energy levels and magnetic moments for ytterbium (f^{13}) and cerium (f^1) ions as a function of spectroscopic and other parameters, using a crystal field model. Values of the parameters were determined to fit experimentally measured susceptibilities. Subsequently, these authors systematically extended[7] this work to other lanthanide ions: terbium (f^8), neodymium (f^3), erbium (f^{11}), thulium, (f^{12}), europium (f^6), praseodymium (f^2), and dysprosium (f^9). Similar calculations on lanthanides were recently present-

ed by Golding and Pyykkö.[8] Using a generalization of a theory developed by Bleaney,[9] pseudocontact shifts and their temperature dependence were calculated and compared to experiment. Bleaney[9] used a spin hamiltonian to take into account zero field splitting due to the crystal field. His theory considers only the thermally accessible states, but corrections for neglect of higher states in the high-frequency susceptibility are estimated. The sign of D and relative magnitudes for different lanthanides are predicted and experimental evidence confirms the predictions.

Extensive ligand field calculations on tetragonal low-spin cobalt(II) phthalocyanine derivatives were performed by Engelhardt and Green.[10] (Our compounds are tetragonal high-spin.) Kurland and McGarvey[11] carried out calculations of pseudocontact shifts for some theoretically simple cases to illustrate their theoretical discussion. McGarvey[12] used the Kurland–McGarvey formulas (see below) to calculate contact and pseudocontact shifts in trigonal Co(II) complexes. As we do below, McGarvey found the high-frequency terms comparable in size to the g factor terms. Using values of spin–orbit coupling parameters and energy level splittings employed by Jesson[13] for related compounds, McGarvey[12] calculated D at 30° in good agreement with a measured value. Contributions of excited electronic energy levels (except those from the lowest crystal field terms) were neglected, as we do below. Jesson[13] had, in an ad hoc way, corrected g values to take this into account and also corrected the spin–orbit coupling for covalency, but McGarvey found the corrections largely cancelled. LaMar et al.[14] measured temperature dependence of shifts and found excellent agreement with McGarvey's results.

Their studies, of the temperature dependence of pseudocontact shifts in trigonal Co(II) complexes, considered particularly the deviations from a Curie law (D proportional to T^{-1}). They emphasized that one must have results at a series of temperatures in order to demonstrate agreement of theory with experiment, as they did using McGarvey's theory.[12] The temperature dependence of pseudocontact shifts due to $Yb(DPM)_3$ was studied by Beauté et al.,[15] who found that straight lines were obtained by plotting shifts vs. $T^{-1/2}$, and that there always existed a value of T for which the shifts were nearly zero. They explained the $T^{-1/2}$ behavior in terms of formation of a collision-type complex. Perry and Drago,[16] discussing the temperature dependence of contact shifts, considered a number of possible causes for nonzero intercepts in plots of shifts against T^{-1}.

For some trigonal Co(II) systems, Jesson[17] calculated D using values for g factors obtained from solid state EPR data. He noted the importance of thermal population of low-lying states but did not consider high-frequency terms in the susceptibility. Other workers have continued to use this technique, although possible sources of error in using solid-state data for species in solution are recognized. Pseudocontact shifts for tetrahedral Ni(II) and Co(II) complexes, low-spin trigonal Co(II) complexes, as well as other species, have thus been predicted.[18] Data on magnetic properties from EPR and on level spacings from spectroscopy may also be used for such predictions, and good agreement with experiment is found.[14]

In the next section, we review the theory needed for the calculation of pseudocontact shifts due to Co(II) in a tetragonal environment, in the framework of a crystal field model. Subsequent sections give analysis of the secular equations with an aim of showing how the calculated values of D arise from crystal field and other parameters. In section V, we consider the dependence of D on temperature and give some results of a complete calculation.

II. Theory

The basic theory of the pseudocontact shifts for tumbling molecules was formulated by McConnell and Robertson.[19] Additions to the theory, to take into account different relative time scales for electronic relaxation, molecular tumbling, and the Zeeman anisotropy energy; high-frequency terms in the susceptibilities; and thermal population of excited states, were given by LaMar,[20] by Jesson,[21] and by Kurland and McGarvey.[11] Different formulas for the pseudocontact shift, differing in the expression for the dipolar field strength, are obtained for different relative time scales. Because of the fast electronic relaxation, the Co^{2+} complexes discussed in the present work fall under the "solid-state" case, wherein $1/\tau \ll |g_\parallel - g_\perp|\mu_B/H\hbar^{-1}$ and $T_1e \ll \tau$. Here, τ is the tumbling correlation time, T_1e the electronic relaxation time, $g_\parallel - g_\perp$ the anisotropy in g factors, and μ_B the Bohr magneton.

Kurland and McGarvey,[11] following an earlier suggestion by Horrocks et al.,[22] gave the dipolar field strength in terms of the principal components of the magnetic susceptibility, and emphasized the importance of the paramagnetic, or high-frequency terms. They carried out calculations for orbital singlets. Their theory, which was extended and used successfully by McGarvey[12] (see preceding section), included thermal population of several states, zero-field splitting, and a ligand contribution to the pseudocontact shift. Horrocks et al.[22] investigated components of the susceptibility for some Co compounds, including measurements of the solid state, wherein the parallel and perpendicular components can be measured separately. Forster[5] obtained pseudocontact shift data for trans $Co(py)_4X_2$ and $Co(\gamma\text{-pic})_4X_2$ complexes, and deduced $g_\parallel > g_\perp$ for X = Cl or NCS, $g_\parallel < g_\perp$ for X = I or Br. Buckingham and Stiles[23] generalized the pseudocontact shift formulas to include higher magnetic moments than dipole moments.

We shall consider only magnetic dipoles, but include thermal population of excited levels and the temperature-independent terms in the susceptibility. The agreement of the experimental results of LaMar et al.[14] on trigonal Co(II) complexes with the calculations[12] based on the Kurland–McGarvey theory[11] shows that both effects make extremely important contributions. Presumably, our system really possesses axial symmetry, so that complications due to deviations from such symmetry[21,24] are ignored.

With the values of time constants that obtain for our systems, the origin of the pseudocontact shifts may be thought of as follows. For each orientation of the molecule in the magnetic field, a magnetic dipole moment, proportional to the field and to the magnetic susceptibilities, is induced at the paramagnetic center (metal ion), which in turn leads to an additional magnetic field at a proton. Because of the asymmetric environment of the paramagnetic center, the induced moment is generally not in the direction of the field, and averaging over all orientations of the molecule does not lead to a zero result. Instead, one obtains a net shift proportional to the asymmetry of the magnetic susceptibility of the paramagnetic center.

In general, the pseudocontact shift for a proton in a molecule becomes a product of a geometric factor, which depends on the proton's position, and a dipolar field factor, which is the same for all protons in the molecule. The latter factor is the subject of our calculations; for our systems,

this requires the anisotropy of the magnetic susceptibility, $\chi_\parallel - \chi_\perp$, where $\parallel$ and $\perp$ refer to the fourfold symmetry axis of the monosubstituted tetragonal complex.

The susceptibilities have temperature-independent (high-frequency) and temperature-dependent (g factor) parts for a given electronic state. The formula (eq 2) for the

$$\chi_\parallel - \chi_\perp = \frac{J(J+1)(g_\parallel^2 - g_\perp^2)\mu_B^2}{3kT} + \sum_j{}'2\,\frac{|\langle j|L_z + 2S_z|i\rangle|^2 - |\langle j|L_x + 2S_x|i\rangle|^2\mu_B^2}{E_j - E_i} \quad (2)$$

anisotropy of the susceptibility for a single state must in general be multiplied by a Boltzmann weighting factor and summed over occupied states. In eq 2, J is the effective spin for a level and will generally be ½ (Kramers' doublet), μ_B is the Bohr magneton, and the sum is over states j not including i, with energy E_j. Also, $g_\parallel$ and $g_\perp$ are the g values for the state in the parallel and perpendicular directions, while L_z and S_z(L_x and S_x) are the orbital and spin angular momentum operators in the parallel (perpendicular) directions. The diamagnetic contributions to the susceptibilities have been ignored; they are easily shown to be very small compared to the others.

The formalism needed for computation of $\chi_\parallel - \chi_\perp$ in the case of high-spin tetragonal Co^{2+} complexes (as well as complexes with trigonal symmetry) has almost all been given by Abragam and Pryce.[25] The Co^{2+} ion, with seven d electrons, has a ^4F ground term, and a relatively low-lying ^4P term (~14,000 cm^{-1} above the ground term) arising from the same configuration. In the presence of an octahedral field, there is significant mixing of the three states of the ^4P term (of orbital symmetry T_{1g}) with the states of the ^4F term. When a tetragonal field is added, one obtains two low-lying energy levels, one singly degenerate and one doubly degenerate, from the lowest T_{1g} state. The effect of spin–orbit coupling on the 12 states arising from the coupling of the two low-lying levels with the spin quartet is to give six Kramers' doublets, spread over an energy range of the order of 10^3 cm^{-1}. We will use these states for the calculation of $\chi_\parallel$ and $\chi_\perp$.

Let us consider the above with attention to the parameters that enter. The difference in energy between the free ion ^4P and ^4F terms is designated by Abragam and Pryce[25] (henceforth referred to as AP) as E_p; a more common nomenclature is $15B$. The parameters for the crystal field used by AP are G (for the octahedral field), H, and I (for the tetragonal part). In terms of the more usual quantities[26] for describing a tetragonal field

$$G = 21Dq - (49/4)Dt$$

$$H = (7/2)Ds$$

$$I = (35/8)Dt$$

If one agrees to use the free-ion value for B and the value obtained for the octahedral hexamethanol complex for Dq, two free parameters, describing the degree of tetragonality, remain. It is common to obtain Dt from the Dq values of the axial (z) and equatorial (x) ligands in a monosubstituted octahedral complex according to the formula[27]

$$Dt = \frac{2}{7}(Dq_x - Dq_z) \quad (3)$$

Unfortunately, in the present case Dq values for the ligands considered are insufficiently known with Co^{2+}. The parameter Ds can be shown to be proportional to Dt for a simple point charge model,[28] the constant of proportionality depending on the metal; we have estimated $Ds \sim 1.42Dt$. Such a proportionality holds in the vast majority of cases that have been studied, but exceptions to the rule exist as well.[29]

In terms of the parameters Dq, Ds, Dt, and B, the two secular equations of AP are given in eq 4a and 4b. The orbital functions π arise from the excited P term and the others from the F term, with ϕ being the T_{1g} species and ψ the T_{2g} species. The ϕ_y, π_y, and ψ_y functions of course have a secular equation identical with the x; the remaining two functions (χ and ψ in AP's notation) are of symmetries A_{2g} and B_{1g} and hence not mixed in the tetragonal field. The solution of the secular equations gives, as wave functions for the lowest level of each secular equation

$$\begin{array}{c|cc} & \phi_z & \pi_z \\ \hline \phi_z & -6Dq + 6Dt - \frac{4}{5}Ds & 4Dq - 4Dt + \frac{12}{5}Ds \\ \pi_z & 4Dq - 4Dt + \frac{12}{5}Ds & 15B + \frac{14}{5}Ds \end{array} \quad (4a)$$

$$\begin{array}{c|ccc} & \phi_x & \pi_x & \psi_x \\ \hline \phi_x & -6Dq + \frac{9Dt}{4} + \frac{2}{5}Ds & 4Dq - \frac{3}{2}Dt - \frac{6}{5}Ds & -\sqrt{\frac{3}{5}}\left(Ds + \frac{5}{4}Dt\right) \\ \pi_x & 4Dq - \frac{3}{2}Dt - \frac{6}{5}Ds & 15B - \frac{7}{5}Ds & -\sqrt{\frac{3}{5}}\left(2Ds + \frac{5}{2}Dt\right) \\ \psi_x & -\sqrt{\frac{3}{5}}\left(Ds + \frac{5}{4}Dt\right) & -\sqrt{\frac{3}{5}}\left(2Ds + \frac{5}{2}Dt\right) & 2Dq + \frac{7}{4}Dt \end{array} \quad (4b)$$

$$\phi_x' = \epsilon\phi_x - \tau\pi_x - \rho\psi_x, \text{ energy } E_x \quad (5a)$$

$$\phi_z' = \epsilon'\phi_z - \tau'\pi_z, \text{ energy } E_z \quad (5b)$$

The energy difference $E_z - E_x$ is denoted by Δ.

The perturbation hamiltonian for spin–orbit coupling, $\lambda\mathbf{L}\cdot\mathbf{S}$, is now introduced. The value of the spin–orbit coupling constant λ is so far not known. One has to diagonalize $\lambda\mathbf{L}\cdot\mathbf{S}$ over the 12 states formed from coupling ϕ_x', ϕ_y', and ϕ_z' with the spin states for $m_s = \pm 1/2$ and $\pm 3/2$. By forming from ϕ_x' and ϕ_y' the symmetric and antisymmetric combinations, AP achieve a simplification in the secular equation. If the symmetric and antisymmetric combinations are assigned fictitious magnetic quantum numbers m_l of 1 and −1, and ϕ_z' the quantum number m_l of 0, the spin–orbit operator, operating on these 12 states, may be shown to be equivalent to

$$-\alpha\lambda L_z S_z - \alpha'\lambda(L_x S_x + L_y S_y)$$

with

$$\alpha = \frac{3}{2}\epsilon^2 - \sqrt{15}\epsilon\rho + \frac{1}{2}\rho^2 - \tau^2 \quad (6a)$$

$$\alpha' = \frac{3}{2}\epsilon\epsilon' + \frac{1}{2}\sqrt{15}\epsilon'\rho - \tau\tau' \quad (6b)$$

The effective hamiltonian is written as

$$W = \Delta(1 - L_z^2) - \alpha\lambda L_z S_z - \alpha'\lambda(L_x S_x + L_y S_y) \quad (7)$$

The 12 × 12 matrix of W actually breaks down into six blocks, corresponding to values of m, the eigenvalue of $L_z + S_z$, equal to 5/2, 3/2, 1/2, −1/2, −3/2, −5/2. The dimensions of the blocks are, respectively, 1, 2, 3, 3, 2, 1; and the first three are identical with the last three.

At this level, there are thus three parameters: Δ, $\alpha\lambda$, and $\alpha'\lambda$. The free-ion value of λ is about -180 cm^{-1}, while α and α' turn out to be about 1.4. Of course Δ, α, and α' are calculable from a knowledge of B, Dq, Ds, and Dt. It is well known that in using the ligand field model it is generally necessary to reduce λ from the free ion value.[26,30] A reduction of about 20% for Co^{2+} seems appropriate.[30]

It is convenient to express energies in units of $\alpha\lambda$ (a negative quantity). Letting $d = \Delta/\alpha\lambda$ and $c = (\alpha'/\alpha) - 1$, the secular equations have the following forms (the states are labeled with m_l and m_s):

$$m = \pm\frac{5}{2}: \left[-\frac{3}{2}\right] \pm 1 \pm\frac{3}{2} \quad (8a)$$

$$m = \pm\frac{3}{2}: \begin{bmatrix} d & -\sqrt{\frac{3}{2}}(c+1) \\ -\sqrt{\frac{3}{2}}(c+1) & -\frac{1}{2} \end{bmatrix} \begin{matrix} 0 & \pm\frac{3}{2} \\ \pm 1 & \pm\frac{1}{2} \end{matrix} \quad (8b)$$

$$m = \pm\frac{1}{2}: \begin{bmatrix} \frac{3}{2} & -\sqrt{\frac{3}{2}}(c+1) & 0 \\ -\sqrt{\frac{3}{2}}(c+1) & d & -\sqrt{2}(c+1) \\ 0 & -\sqrt{2}(c+1) & \frac{1}{2} \end{bmatrix} \begin{matrix} \pm 1 & \pm\frac{3}{2} \\ 0 & \pm\frac{1}{2} \\ \pm 1 & \pm\frac{3}{2} \end{matrix} \quad (8c)$$

The anisotropy is expressed by the values of c and d; in octahedral symmetry $c = d = 0$. The state of lowest energy corresponds to the highest eigenvalue of these matrices. Clearly, the higher eigenvalue for $m = \pm 3/2$ is higher than that for $m = \pm 5/2$, while that for $m = \pm 1/2$ is the highest, as can be seen by comparing its upper left 2 × 2 block with the $m = \pm 3/2$ submatrix. Therefore, the lowest energy, which is obtained from the eigenvalue by multiplication by the negative quantity $\alpha\lambda$, arises from the $m = \pm 1/2$ block.

Having determined the six eigenvalues and eigenvectors for the Kramers' doublets, we can use them to calculate $\chi_\parallel$ and $\chi_\perp$ for any of them by eq 2. The g values are simply

$$g_\parallel = 2\langle i_+ | L_z + 2S_z | i_+ \rangle \quad (9a)$$

$$g_\perp = 2\langle i_+ | L_x + 2S_x | i_- \rangle \quad (9b)$$

where i_+ and i_- are the two members of the Kramers' doublet. A correction must be made to take into account mixing in, by the spin–orbit coupling, of orbital states with energies above the ϕ' states (eq 5). This is discussed by AP, who find corrections of a few percent, which represents the size of the ratio of $|\alpha\lambda|$ to the energy difference, i.e. ~250/9000. We shall neglect these corrections to $g_\parallel$ and $g_\perp$ (see ref 25, 12, and 13). Correspondingly, we neglect contributions of higher orbital states to the high-frequency terms of the susceptibility, so that both i and j in eq 2 will always be members of the set of six Kramers' doublets. This and the use of a crystal field formalism are the basic approximations in our calculations.

To go from the parameters Ds and Dt to susceptibilities requires, in the present models, solution of two secular equations. The first is eq 4, and produces calculated values of α, α', and Δ, from which $c = (\alpha'/\alpha) - 1$ and $d = \Delta/(\alpha\lambda)$ are calculated; this will be discussed in section III. The second secular equation, eq 8, leads to wave functions from which magnetic properties are calculated, and will be considered in section IV.

III. The Parameters c and d

We consider the secular eq 4 for ϕ_x' and ϕ_z', assuming that values are known for B, Dq, Ds, and Dt. Calculating Dt from estimated values of the substituent and of methanol (eq 3), we find relatively small values for all the cases of interest to us. For example, estimated values[32] of Dq for CH_3OH and γ-picoline are 900 and 1100 cm^{-1}, respectively, so that $Dt = -57$ cm^{-1}. The value of Ds is estimated as $1.42Dt = -81$ cm^{-1} according to an interpolation formula[28] for the Ds/Dt ratio. Similarly, Dt is estimated as 1 cm^{-1} for DMSO and -2 cm^{-1} for H_2O. We can therefore say that we are always dealing with cases of low tetragonality. This allows a perturbative treatment of the effect of Ds and Dt. We first neglect Ds and Dt in (4) and solve the resulting 2 × 2 secular equations, yielding energies E_1 and E_2 ($E_1 < E_2$) and corresponding eigenvectors (coefficients) (a, b) and (b, $-a$). Here, $a^2 + b^2 = 1$. and the values of a and b depend on the values of B and Dq. For the reasonable values, $B = 825$ cm^{-1} and $Dq = 900$ cm^{-1}, $a \sim 0.98$ and $b \sim -0.20$. We now transform the secular equations for x and z to the basis of these eigenvectors.[33] The lowest eigenvalues of each matrix may now be evaluated by perturbation theory to second order. It is in each case the upper left diagonal matrix element plus a sum of squares of first-row off-diagonal elements divided by differences of diagonal elements. In calculating Δ, E_1 cancels out as expected. Performing the necessary algebra we obtain

$$\Delta = a^2\left(\frac{15}{4}Dt - \frac{6}{5}Ds\right) + 2ab\left(-\frac{5}{2}Dt + \frac{18}{5}Ds\right) + b^2\left(\frac{21}{5}Ds\right) \quad (10)$$

after dropping second-order terms in Ds and Dt.

We expect ab to be negative; a^2 and b^2 are of course positive. Let us write K for the ratio Ds/Dt; we expect K to be about 1.4. With $a = 0.98$ and $b = -0.20$, the first-order terms become $(4.5 - 2.4\,K)Dt$. Thus Δ has the sign of Dt unless K is unexpectedly large and positive. With $K = 1.42$, Δ has about the numerical value of Dt. That the first-order terms suffice is shown by the case of γ-picoline, for which the exact calculation for $K = 1.42$, using the secular equations, gave $\Delta = -66$ cm^{-1}, while the above formula yields -68 cm^{-1}. It may be repeated that Δ and Dt will not have the same signs if K is greater than 1.9, as is the case[31] for Cu^{2+}.

We now consider the α' to α ratio and the value of c by a similar method. The coefficients ϵ, τ, ρ, ϵ', and τ' are computed by first-order perturbation theory. The eigenfunctions, written as column vectors, are, from (4a) for ϕ_z'

$$\begin{pmatrix} a \\ b \end{pmatrix} + \frac{ab\left(6Dt - \frac{18}{5}Ds\right) + (b^2 - a^2)\left(-4Dt + \frac{12}{5}Ds\right)}{E_1 - E_2}\begin{pmatrix} b \\ -a \end{pmatrix} \quad (11a)$$

and, from (4b) for ϕ_x'

$$\begin{pmatrix} a \\ b \\ 0 \end{pmatrix} + \frac{ab\left(\frac{9Dt}{4} + \frac{9Ds}{5}\right) + (b^2 - a^2)\left(\frac{-3Dt}{2} - \frac{6Ds}{5}\right)}{E_1 - E_2}\begin{pmatrix} b \\ -a \\ 0 \end{pmatrix} + \frac{-\sqrt{\frac{3}{5}}(a + 2b)\left(Ds + \frac{5}{4}Dt\right)}{E_1 - 2Dq}\begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \quad (11b)$$

From these, the parameters of eq 5 can be read off directly, for evaluation of α and α' using eq 6. We keep terms to first order, and, after considerable algebra, obtain

$$c = \frac{a^2b^2\left(\frac{75}{8}Dt - \frac{27}{2}Ds\right) + (ab^3 - a^3b)\left(9Ds - \frac{25}{4}Dt\right)}{\left(\frac{3}{2}a^2 - b^2\right)(E_1 - E_2)} - \frac{a(a + 2b)\left(\frac{9}{2}Ds + \frac{45}{8}Dt\right)}{\left(\frac{3}{2}a^2 - b^2\right)(E_1 - 2Dq)} \quad (12)$$

For γ-picoline, with the parameter values quoted above, this formula gives $c = -0.033$, to be compared to the exact value (from secular equations) of -0.035.

In considering the sign of c, we find that the expression is dominated by the second term. The denominator is clearly negative, while $a(a + 2b)$ is positive. Therefore c should have the sign of Ds and Dt; if Ds and Dt have different signs, their relative magnitudes determine which sign dominates. With $a = 0.98$, $b = -0.2$, and $Dq = 900$ cm^{-1}, the second term gives

$$c = 23 \times 10^{-5}\left(K + \frac{5}{4}\right)Dt \text{ (cm}^{-1}\text{)} \quad (13)$$

which, for our γ-picoline data, yields $c = -0.035$.

Therefore, we expect c and Δ to have the sign of Ds and Dt. This means c and $d = \Delta/\alpha\lambda$ should have opposite signs. Both c and d may be considered, under these circumstances, as reflecting the relative crystal field strengths of the substituent and methanol.

IV. Susceptibilities for Low Asymmetry

We now turn to the secular eq 8, where both c and d are small compared to unity, signifying that the tetragonality is low. The states used as basis for these secular equations are products of spin functions for spin 3/2 and spatial functions over which the orbital angular momentum matrices are known. The secular eq 8 break down into blocks[25] by $m = m_l + m_s$, and the matrices of $L_z + 2S_z$ and $L_x + 2S_x$ are easily calculable in this basis. The former is diagonal in m, and the latter has nonvanishing elements between functions differing by unity in m.

To obtain the eigenfunctions, we again resort to perturbation theory. If $c = d = 0$ (pure octahedral symmetry) the secular equations may be solved exactly to give the eigenfunctions and energies (m values in parentheses) of Table I. The basis functions are labeled by the eigenvalues m_l and m_s; overbars represent minus. Since $\alpha\lambda$ is negative, the lowest energy is $(5/2)\alpha\lambda$. As long as c and d are small, the presence of tetragonality will not change this. It is now straightforward to transform the matrices of $L_z + 2S_z$, $L_x + 2S_x$, and the effective hamiltonian to the basis of Table I.[33]

TABLE I: Eigenfunctions and Eigenvalues of the Secular Eq 8 for Octahedral Symmetry ($c = d = 0$)

Eigenfunction	Eigenvalue	Value of m
$\lvert 1\frac{3}{2}\rangle$	$\frac{-3}{2}\alpha\lambda$	$\left(\frac{5}{2}\right)$
$\sqrt{\frac{3}{5}}\lvert 1\frac{1}{2}\rangle + \sqrt{\frac{2}{5}}\lvert 0\frac{3}{2}\rangle$	$\frac{-3}{2}\alpha\lambda$	$\left(\frac{3}{2}\right)$
$\sqrt{\frac{2}{5}}\lvert 1\frac{1}{2}\rangle - \sqrt{\frac{3}{5}}\lvert 0\frac{3}{2}\rangle$	$1\alpha\lambda$	$\left(\frac{3}{2}\right)$
$\sqrt{\frac{1}{10}}\lvert \bar{1}\frac{3}{2}\rangle + \sqrt{\frac{6}{10}}\lvert 0\frac{1}{2}\rangle + \sqrt{\frac{3}{10}}\lvert 1\bar{\frac{1}{2}}\rangle$	$\frac{-3}{2}\alpha\lambda$	$\left(\frac{1}{2}\right)$
$\sqrt{\frac{6}{15}}\lvert \bar{1}\frac{3}{2}\rangle + \sqrt{\frac{1}{15}}\lvert 0\frac{1}{2}\rangle - \sqrt{\frac{8}{15}}\lvert 1\bar{\frac{1}{2}}\rangle$	$1\alpha\lambda$	$\left(\frac{1}{2}\right)$
$-\sqrt{\frac{1}{2}}\lvert 1\frac{3}{2}\rangle + \sqrt{\frac{1}{3}}\lvert 0\frac{1}{2}\rangle - \sqrt{\frac{1}{6}}\lvert 1\frac{1}{2}\rangle$	$\frac{5}{2}\alpha\lambda$	$\left(\frac{1}{2}\right)$
$-\sqrt{\frac{1}{2}}\lvert 1\frac{3}{2}\rangle + \sqrt{\frac{1}{3}}\lvert 0\bar{\frac{1}{2}}\rangle - \sqrt{\frac{1}{6}}\lvert \bar{1}\frac{1}{2}\rangle$	$\frac{5}{2}\alpha\lambda$	$\left(\frac{-1}{2}\right)$
$\sqrt{\frac{6}{15}}\lvert 1\bar{\frac{3}{2}}\rangle + \sqrt{\frac{1}{15}}\lvert 0\frac{1}{2}\rangle - \sqrt{\frac{1}{6}}\lvert \bar{1}\frac{1}{2}\rangle$	$1\alpha\lambda$	$\left(\frac{-1}{2}\right)$

Then one can write the eigenfunctions of the secular equations using first-order perturbation theory. Of course, these are expressed in terms of the eigenfunctions for pure octahedral symmetry. For instance, the ground state wave function is

$$\lvert 1\rangle = \left\lvert E = \frac{5}{2},\ m = \frac{1}{2}\right\rangle + \frac{7c + 2d}{9\sqrt{5}}\left\lvert E = 1,\ m = \frac{1}{2}\right\rangle + \frac{c + d}{4\sqrt{5}}\left\lvert E = \frac{-3}{2},\ m = \frac{1}{2}\right\rangle \quad (14)$$

where we have labeled the octahedral eigenfunctions by their energies (in units of $\alpha\lambda$) and their m values. They are given in terms of the original basis by the coefficients in Table I. The g values are easily calculated to this order using the matrices of $L_z + 2S_z$ and $L_x + 2S_x$

$$g_\parallel = 2\langle 1\lvert L_z + 2S_z\rvert 1\rangle = \frac{2}{27}[9(\alpha + 5) - (14c + 4d)(\alpha + 2)] \quad (15a)$$

$$g_\perp = 2\langle 1\lvert L_x + 2S_x\rvert \bar{1}\rangle = \frac{2}{27}[9(\alpha' + 5) + (7c + 2d)(\alpha' + 2)] \quad (15b)$$

The state $\lvert\bar{1}\rangle$ is the degenerate partner of $\lvert 1\rangle$, with $m = 1/2$. For γ-picoline, eq 15 give $g_\parallel = 4.56$ and $g_\perp = 4.323$, which differ by only 0.1% from the values calculated from the full secular equation. When $c = d = 0$ and $\alpha = \alpha'$ (octahedral symmetry), $g_\parallel^2 = g_\perp^2$ as expected. A direct calculation of the anisotropy to first order gives

$$g_\parallel^2 - g_\perp^2 = -(8/27)[(7c + 2d)(\alpha + 5)(\alpha + 2) + 3c\alpha(\alpha + 5)] \quad (16)$$

For γ-picoline, this formula gives -1.428 while the correct value is -1.467. It may be noted that we are here calculating the small difference between two almost equal numbers.

Since c and d are expected to have opposite signs, the sign of eq 16 is not evident. With $\alpha \sim 1.4$, the right side of eq 16 becomes roughly $-53c - 13d$, into which we insert

our approximate expressions for c and d: $d = 1.19Dt/(\alpha\lambda) = -0.0047Dt$, $c = 0.00061Dt$ ($\lambda = -180$ cm^{-1} used here). This gives

$$g_\parallel^2 - g_\perp^2 \sim 0.029Dt \text{ (cm}^{-1}\text{)}$$

which is -1.6 for λ-picoline (exact value, -1.5). If $\lambda = -150$ cm^{-1} is used instead of -180 cm^{-1}, -2.4 is obtained, indicating a high sensitivity of results to the value of this parameter.

We turn to calculation of the second term in eq 2, the "high-frequency terms". The matrix elements required for $\chi_\parallel$ are between $|1\rangle$ and the other $m = 1/2$ states

$$|2\rangle = \frac{7c + 2d}{-9\sqrt{5}}\left|E = \frac{5}{2},\ m = \frac{1}{2}\right\rangle + \left|E = 1,\ m = \frac{1}{2}\right\rangle + \frac{2d - c}{25}\left|E = \frac{-3}{2},\ m = \frac{1}{2}\right\rangle \quad (17a)$$

and

$$|3\rangle = \frac{c + d}{-4\sqrt{5}}\left|E = \frac{5}{2},\ m = \frac{1}{2}\right\rangle + \frac{2d - c}{25}\left|E = 1,\ m = \frac{1}{2}\right\rangle + \left|E = \frac{-3}{2},\ m = \frac{1}{2}\right\rangle \quad (17b)$$

A direct calculation gives

$$\frac{1}{2}\chi_\parallel^{hf} = (\alpha + 2)^2\left(\frac{10}{27} - \frac{23c + 7d}{81}\right)$$

This formula gives 4.195 for γ-picoline; the directly calculated value (via the secular equation) is 4.213. For the high-frequency part of $\chi_\perp$, we need matrix elements between $|1\rangle$ and the functions $|\bar{2}\rangle$ and $|\bar{3}\rangle$ (for $m = -1/2$) as well as the functions for $m = 3/2$. After lengthy algebra, we find

$$\frac{1}{2}\chi_\perp^{hf} = (\alpha' + 2)^2\left(\frac{10}{27} + \frac{7d - 37c}{162}\right)$$

which gives 4.436 for λ-picoline, to be compared with 4.480 from complete solution of the secular equation. Putting $\alpha' = \alpha(1 + c)$, we find

$$\chi_\parallel^{hf} - \chi_\perp^{hf} = \frac{(\alpha + 2)^2}{81}\left(-9c - 21d - 120\frac{c\alpha}{\alpha + 2}\right) \quad (18)$$

which gives -0.564 for this data, to be compared with the directly calculated value of -0.534. All the high-frequency terms are in units of $\mu_B^2/|\alpha\lambda|$. Like $g_\parallel^2 - g_\perp^2$, (18) represents a small difference between large numbers.

The dipole strength is given by

$$D = \frac{1}{3}(\chi_\parallel - \chi_\perp) = \frac{(g_\parallel^2 - g_\perp^2)\mu_B^2}{12kT} + \frac{\chi_\parallel^{hf} - \chi_\perp^{hf}}{|\alpha\lambda|}\frac{\mu_B^2}{3} \quad (19)$$

since $J = 1/2$ here, and we calculate $\chi_\parallel^{hf}$ and $\chi_\perp^{hf}$ as dimensionless quantities. If we use cgs units, for which the Bohr magneton μ_B is -0.927×10^{-20} erg/Oe, and express $|\alpha\lambda|$ in cm^{-1} and T in degrees, eq 19 becomes

$$D = 1.44 \times 10^{-25}\left[\frac{g_\parallel^2 - g_\perp^2}{(T/1.44)} + \frac{\chi_\parallel^{hf} - \chi_\perp^{hf}}{|\alpha\lambda|}\right] \text{ cm}^3 \quad (20)$$

For the moment, we have been considering the signs of the first and second terms of (20). We have argued that c and d are probably of opposite sign, and showed that $g_\parallel^2 - g_\perp^2$ is roughly $-53c - 13d$, and $\chi_\parallel^{hf} - \chi_\perp^{hf}$ roughly $-7c - 2.9d$. With the values suggested earlier for $K = Ds/Dt$ (1.42) and $\alpha\lambda$ (1.4×180 cm^{-1}), we find $d = -0.0047Dt$ and $c = 0.00067Dt$ with Dt expressed in cm^{-1}. Then $g_\parallel^2 - g_\perp^2 \sim 0.029Dt$ and $\chi_\parallel^{hf} - \chi_\perp^{hf} \sim 0.0094Dt$, i.e., both anisotropies are of the same sign. This means that there is no positive temperature T for which the dipole field factor D vanishes. Thus, if the pseudocontact shifts for cis and trans methanol protons were plotted against reciprocal temperature, they would *not* cross at any positive temperature. However, we have assumed population of only one Kramers' doublet, which is valid only at low temperatures.

For $\lambda = -180$ and $\alpha\lambda$ about -250 cm^{-1}, the energy difference between ground and first excited state is $-(3/2)\alpha\lambda \sim 380$ cm^{-1}. The Boltzmann factor at 200°K would be 0.066 and at 300°K it would be 0.16. Thus the importance of excited states is not negligible, since $|\lambda|$ is probably smaller than 180 cm^{-1} for the complexed ion (it is 150 cm^{-1} for tetrahedral Co^{2+} complexes) and $g_\parallel^2 - g_\perp^2$ can be much larger than 1.5 for the excited states.

V. Effect of Temperature

The effects of thermal population are considered in this section, as we study the variation of D with temperature. After working out several limiting cases, we show how the experimental results for the γ-picoline complex are explained by the crystal field calculation. In all the calculations, we consider only the lowest 12 states, formed by coupling the two lowest-lying orbital levels, one of which is doubly degenerate, with the spin quartet. Thermal population of other levels is negligible, while their contribution to χ^{hf} is only a few percent of the contribution of the lowest 12 states, as discussed in section I.

Experimental results from which one can determine D as a function of T are available for several systems.[4] We derive D from the shifts of the cis and trans methanol protons of the pentakis(methanol) complex by formulas given in our previous article.[3,34] Over the temperature range studied, the shifts, plotted against T^{-1}, are fit to within experimental error by straight lines. In Table II we give the coefficients a and b in the formula,

$$D = a + bT^{-1} \quad (21)$$

as determined by least-squares fits of the cis and trans shifts. Since a and b have opposite signs, extrapolation of the straight line would lead to a value of T for which D vanishes (see Table II).[35]

In fact, calculations (see below) show that such an extrapolation is not meaningful because the straight-line character of the D vs. T^{-1} plot is only apparent, due to the limited temperature range. This is shown already by simple calculations in the limiting cases corresponding to small spin–orbit coupling, which we perform first. Small values of the spin–orbit coupling constant λ mean that d becomes large compared to c, so this may also by referred to as the high d limit. For the case treated[25] by Abragam and Pryce, $Co(NH_4)_2(SO_4)_2 \cdot 6H_2O$ in the crystal, the values $c = 0.3334$ and $d = -5.373$ are suggested, so that $d/c \sim -16$ and the high d limit should be applicable. Our interest in this limit at present is that it allows explicit formulas for the temperature dependence.

When $|d|$ is large compared to c, we may ignore matrix elements in the secular equations which couple states for which the diagonal elements differ by d, since all these matrix elements are proportional to c. This means that the

TABLE II: Experimentally Determined Dipole Strengths as a Function of Temperature (see Eq 21) for $Co(CH_3OH)_5X^{2+}$ Complexes

Ligand X	Dt (est), cm^{-1}	Temp range, °C	$10^{28}b$	$10^{28}a$	D at 222°K	Crossing, °K
Pyridine	−60	−98 to −10	−7667	19.05	-15.5×10^{-28}	402
γ-Picoline	−57	−81 to −40	−7014	19.30	-12.3×10^{-28}	363
H_2O	−4	−85 to −1	3640	−9.24	7.2×10^{-28}	394

matrices are effectively diagonal. We must consider separately what happens for positive d and for negative d.

In the latter case, the eigenenergies, in order of increasing energy, are 3/2, 1/2, −1/2, −3/2, d, d (remember that energies are in units of the negative quantity $\alpha\lambda$), with corresponding eigenstates $|\pm1 \mp 3/2\rangle, |\pm1 \mp 1/2\rangle, |\pm1 \pm 1/2\rangle, |\pm1 \pm 3/2\rangle, |0 \pm 3/2\rangle, |0 \pm 1/2\rangle$. Since we consider d to be large, we can neglect the populations of the last two states. Their contribution to the high-frequency terms in the susceptibilities will also be ignored, because of the large energy denominators. The value[36] of $g_\perp$ (see eq 9) is zero for the other four states because $L_x + 2S_x$ can couple only states differing by unity in *either* m or m_s. Because the matrix of $L_z + 2S_z$ over these states is diagonal, $\chi_\parallel^{hf}$ is identically zero for all four states.

If only the ground state is considered, $g_\parallel^2 - g_\perp^2$ and $\chi_\parallel^{hf} - \chi_\perp^{hf}$ have opposite signs, and a crossing ($D = 0$) occurs in plots of cis and trans pseudocontact shifts vs. $1/T$. The full expression for D involves calculating $\chi_\parallel - \chi_\perp$ for each of the four states and weighting each with a Boltzmann factor. This yields

$$D = \frac{(\alpha + 3)^2 + (\alpha + 1)^2P + (\alpha - 1)^2P^2 + (\alpha - 3)^2P^3}{3kT(1 + P + P^2 + P^3)} + \frac{6 + 2P - 2P^2 - 6P^3}{3\alpha\lambda(1 + P + P^2 + P^3)} \quad (22)$$

where $P = \exp(\alpha\lambda/kT)$. D of eq 22 never becomes zero. Since the plot of D vs. T^{-1} goes through the origin but has an increasing slope with increasing T^{-1}, extrapolation of any portion, after fitting to a straight line, will give an apparent crossing.

If d is large and negative, there are two low-lying doublets, and the other four doublets, with energies lying above these by d, should be dropped from consideration. However, the two states have the same energy, namely, $d\alpha\lambda$, in the limit. We thus must consider mixing of other states to split the degeneracy. According to perturbation theory, the state $|0 \pm 1/2\rangle$ now has an energy in units of $\alpha\lambda$ of $d + 3/2(c + 1)^2/d + 2(c + 1)^2/d$, and the state $|0 \pm 3/2\rangle$ has an energy of $d + 3/2(c + 1)^2/d$. With the abbreviation $u = 2(c + 1)^2\alpha\lambda/dkT$, we calculate

$$D = \frac{-12 + 36e^u}{12(1 + e^u)kT} + \frac{-6 + 6e^u}{3(1 + e^u)ukT}$$

which becomes $(4 + u)/2kT$ for sufficiently small u. Apparently, a plot at high temperatures would not be of the familiar form $a + bT^{-1}$, but rather $aT^{-2} + bT^{-1}$. The T^{-2} term arises from the near degeneracy.[9] Now suppose $c \sim 0$, $\alpha\lambda \sim 250$ cm^{-1}, and $d = 10$; then $u = -72/T$ (degrees). For temperatures of 100, 150, 200, and 250°, the values of D are 0.0127, 0.0101, 0.0082, and 0.0068, respectively, in units of μ_B^2/k. Plotting these against T^{-1}, one obtains reasonable "straight lines" which can be extrapolated to $D = 0$ at about 500°. In fact, the lines are not straight, and direct calculation shows that D never vanishes. Actually, the $a + b/T$ dependence due to the contribution of a single state to D is probably masked by Boltzmann factors, and the crossings of cis and trans pseudocontact shifts as extrapolated from plots vs. T^{-1}, have no real significance.

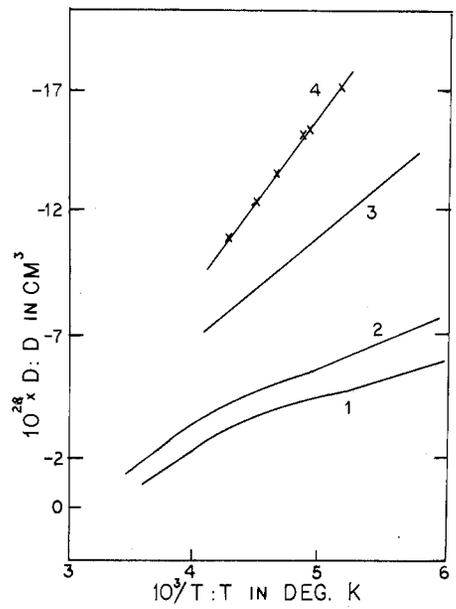

Figure 1. Dipole strength factor (D in $cm^3 \times 10^{28}$) for λ-picoline as a function of temperature ($10^3/T$, T in degrees Kelvin). Curve 1 is calculated with $Dq = 900$ cm^{-1}, $Dt = -57$ cm^{-1}, $Ds = -81$ cm^{-1}, $B = 825$ cm^{-1}. Curve 2 results when λ is changed from -180 cm^{-1} (curve 1) to -150 cm^{-1}. Curve 3 results on changing Dt to -100 cm^{-1}, maintaining the Ds/Dt ratio. Curve 4 is a straight-line fit to the experimental points, shown as X's.

We have carried out extended calculations of D values, starting from assumed values for Ds and Dt, generating α, α', and Δ, and thence calculating g values and susceptibilities. It is possible to fit the measured values of D as well as their temperature dependence, using reasonable values of the parameters Ds, Dt, and λ. This is not too surprising, perhaps, but it shows that one can discuss and explain observed Co^{2+} pseudocontact shifts in the framework of the crystal field model.

For example, we give the results of complete calculations for a single case, λ-picoline, to show the nature of the temperature dependence and how it is fit by our calculations. The parameters used first are: $\alpha = 1.4355$, $\alpha' = 1.3849$, and $d = 0.2554$ (corresponding to $\lambda = -180$ cm^{-1}). In each case, population of three states is taken into account. A second set of calculations was made using the more reasonable value of -150 cm^{-1} for λ. Results of the two are shown in Figure 1. A high value of $g_\parallel^2 - g_\perp^2$ for the first excited state (with $m' = 3/2$ and thus $g_\perp = 0$) meant that, even with a small population, it gave an important contribution to the g factor term. The value of D is obtained in cm^3 from the numerical value of our expression by multiplication by $(1/3)\nu_0\mu_B^2/k$, where k is the Boltzmann constant, μ_B the

Bohr magneton (0.927×10^{-20} erg/Oe), and ν_0 the NMR frequency (100 MHz in our case).

The experimental values (which are obtained from measured frequencies using a geometrical factor which may be inaccurate due to errors in the assumed geometries) are also plotted (curve 4). Several observations may be made. First, both results give D values of the right sign and having the right temperature dependence. Over the temperature range of the experimental data, the calculated points give a satisfactory straight line on a plot vs. reciprocal temperature. However it would be a grave error to assume that D was of the $a + b/T$ form and extrapolate to the point for which $d = 0$. Thermal population of excited states is actually extremely important.

Another calculation, in which Dt was changed from -57 to -100 cm^{-1}, but $\lambda = -150°$ and $Ds/Dt = 1.4$ were maintained, gave much improved results (see Figure 1, curve 3). The magnitude of D and the slope of the D vs. T^{-1} plot are both significantly increased. The change of 43 cm^{-1} in Dt corresponds to a change of 150 cm^{-1} in the difference of Dq values for methanol and λ-picoline. Since each Dq is about 1000 cm^{-1}, such a change is within the range of our ignorance. Finally, we experimented with changing the Ds to Dt ratio. As our analysis of section II showed, the parameters d and c and hence our results depend strongly on this ratio and a change of a few tenths from the value of 1.4 can move our calculated points above the experimental ones. It is clear from these experiments that, with a reasonable choice of parameters, our model can fit observed data for D of λ-picoline.

Similar numerical experiments have convinced us that fits are similarly obtainable for other systems. Given the inaccuracies of the model and the uncertainty in the value of the parameters, it does not seem valuable to present such results and attempt to choose "correct" values of Ds, Dt, and λ. Only if one of these parameters were independently measured, would it become worthwhile to find the values of the other two required by the experimental results.

Our theoretical work shows that the crystal field model can be used to reproduce and explain pseudocontact shifts and their temperature dependence for the $Co(CH_3OH)_5X^{2+}$ systems and, by implication, for other tetragonal high-spin Co(II) systems. However, our results warn against naive interpretations of the apparent linearity of shifts when plotted against T^{-1}, or extrapolation to a point for which D vanishes. A theory for these shifts must include thermal population of low-lying states, and straight lines on plots of shifts vs. T^{-1} are not be be expected.

The correlation of shifts with crystal field parameters, and particularly with the sign of Dt, is dangerous as well. Such correlations require that Ds/Dt be neither too large nor negative. For all cases of interest to us, simple expressions are now available giving the anisotropy of the low-lying states, as expressed by c and d, in terms of the crystal field parameters. Calculation of D in terms of c, d, λ, and the temperature requires more involved calculations.

Supplementary Material Available. The matrices of the effective hamiltonian, $L_z + 2S_z$, and $L_x + 2S_x$, transformed to the basis of Table I will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number JPC-75-1206.

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(32) Values for Dq for H_2O and DMSO in Co(II) complexes are available in ref 26, but not for other ligands. Such Dq values are given for Ni(II) tetragonal complexes. We estimate their values for the Co(II) complexes by multiplying the Ni(II) values by 1.09, which is the ratio of Co to Ni Dq values for H_2O and DMSO.

(33) See paragraph at end of text regarding supplementary material.

(34) The definition of D used in the present work, eq 1, conforms more closely to current practice than that of ref 3. The values of D given in ref 3 include a factor of ν_0, and should therefore be divided by 10^8 to yield the values in this paper. Note that we are now using ångströms for units of length.

(35) Corresponding results have been obtained for other systems (J. Vriesenga, private communication), for which X = α-picoline, β-picoline, 3-chloropyridine, 3-cyanopyridine, acetonitrile, dimethyl sulfoxide, etc.

(36) The g values and high-frequency susceptibilities are given in the microfilm edition of this volume of the journal. See paragraph at end of text for details.